JET FUEL SYSTEM ICING INHIBITORS: SYNTHESIS AND STABILITY

[a,b]George W. Mushrush, [b]Erna J. Beal, [b]Dennis R. Hardy, [a]Wayne M. Stalick, [a]Subhash Basu, [c]Dennis Grosjean, and [d]John Cummings

[a]George Mason University, Fairfax, VA 22030, [b]Navy Technology Center for Safety and Survivability, Washington, DC 20375, [c]Innovative Scientific Solutions Inc., 2786 Indian Ripple Road, Dayton, OH 45440, and [d]Naval Air-Warfare Center, Trenton, NJ 08628

ABSTRACT

The current fuel system icing inhibitor additives, used both by the military and commercial aviation, are ethylene glycol monomethyl ether (EGME) and diethylene glycol monomethyl ether (DiEGME). These deicing compounds are toxic at the concentrations that are required for effective deicing. This observation points to an immediate need for non-toxic, inexpensive, and biodegradable deicing compounds. The synthesis of polar sugar derivatives represents viable alternatives to glycol based additives. The synthesis and characterization of acetals, ketals, ethers, and esters of oxoacids will be discussed. These alternative deicing compounds are cheap, fuel stable, and exhibit similar icing inhibitor characteristics to EGME and DiEGME.

INTRODUCTION

The literature of deicing additives for jet fuels is rather sparse. Those articles that have appeared are related to concentration determination, stability in fuels, and health implications of these additives(1, 2). Currently the fuel icing inhibitor additives, ethylene glycol monomethyl ether (EGME) and diethylene glycol monomethyl ether (DiEGME), are mandatory in all military aircraft fuels and are optional in world-wide commercial aviation fuels depending on route, flight length, and season. Unfortunately, ethylene glycol based deicing compounds are toxic at the concentrations that are required for effective deicing (2). These additives are leached out of the fuel and into water bottoms and when this water is drained from fuel system sumps, filters and storage tanks it contains EGME and/or DiEGME thus creating a personnel health hazard. Also, glycols exert high oxygen demand for decomposition and when they get into the environment they cause the death of aquatic organisms as dissolved oxygen is depleted. These observations all point to an immediate need for non-toxic, inexpensive, and biodegradable deicing compounds. The approach of our laboratory is to utilize the large U.S. surplus of sugars as the basis for the synthesis of biodegradable deicing compounds. These potential deicing candidates must satisfy many constraints. They must be soluble in jet fuel, soluble in water, fuel stable during storage, and exhibit similar or enhanced ice inhibiting characteristics to currently used deicing compounds.

The latter of these constraints, concerning the behavior of deicing compounds in fuels, is being investigated in our laboratory since there are no readily available software programs to estimate either the physical or colligative properties of middle distillate fuels. A large number of physicochemical and toxicological properties are prerequisite to a reasonable hazard assessment of a chemical (1). However, environmental fate, and toxicity of chemicals can be estimated using computer models. These predicted values provide the guidance towards synthesizing safer icing inhibitors for this project.

EXPERIMENTAL

The general synthesis procedure followed for the synthesis of the glycerol acetals and ketals was that reported for the synthesis of the 2,2-dimethyl-1,3-dioxolane-4-methanol, compound I (3). The procedure was modified for the synthesis of the formaldehyde (compound II), and acetaldehyde (compound III), adducts. Acetone (232g, 4.5moles), or acetaldehyde (197g, 4.5 moles), or formaldehyde (135g, 4.5 moles), was added to glycerol (100 g, 1.1 moles) in a toluene solvent (300 mL), containing 3.0 g p-toluene sulfonic acid and 255 g of 5A molecular sieves all in a 2,000 mL two-necked, round-bottomed flask fitted with a mechanical stirrer and a condenser. A freezing mixture of ethylene glycol and water at -25.0 °C was circulated through the condenser. The stirred reaction mixture was heated under gentle reflux for 33 hrs using a heating mantle. After reflux, the condenser was disconnected and excess acetaldehyde was allowed to evaporate. The acidic reaction mixture was neutralized with 3.0 g sodium acetate. The molecular sieves were separated by vacuum filtration using a Büchner funnel. The resulting liquid was distilled under vacuum. The colorless organic product distilling at 80-82?C/10 mm was collected for the acetone derivative to give a yield of 88%; for the acetaldehyde derivative the

product distilling at 85-90 ?C/10mm was collected to give a yield of 80 %; and for the formaldehyde derivative the product distilling at 95-96?C/10 mm was collected (4).

Computational Methods. In order to estimate environmental fate and certain physical properties, a suite of programs developed by Syracuse Research Corporation was used (5). Well established computational methods are used in these programs.

DISCUSSION

The reaction products of aldehydes and ketones with glycerol have been known for more than 100 years. These compounds were usually regarded as intermediates in synthetic procedures and little interest was expressed in them. The compounds in this study are simpler than the. carbohydrates and carbohydrate derivatives so they were the subject of this initial investigation Acetal and ketal formation is catalyzed by either mineral acids or Lewis acids. The intermediate hemi-acetal or hemi-ketal is not usually isolated. The compounds were subjected to testing for deicing characteristics and compared to EGME, DiEGME, and dipropylene glycol. Dipropylene glycol was included because industries and the Federal Aviation Administration have recommended it as a replacement for the ethylene based deicers. The freezing point tests were conducted in a one gallon simulator rig. The data showed that both compounds II and III were effective deicers and closely paralleled the behavior of EGME and DiEGME(6). Compounds II and III show similar time vs temperature dependence The compounds were also tested for fuel instability and incompatibility reactions. They were tested for storage stability by ASTM method D5304-92 in JP-8 (7).

Additives in this Study

These compounds, along with their estimated physical properties and environmental toxicity profile, are presented in Table 1. Compound I appears to have excellent potential properties as a deicing agent. This compound has been well characterized in the literature and is considered to be relatively non-toxic (8). It is used commercially as a solvent, plasticizer, and solubilizing and suspending agent in pharmaceuticals. Additionally, it is miscible in hydrocarbons, gasolines, turpentine, oils, and water; making it an ideal candidate as an icing inhibitor. Although Compound I has a higher dermal dose per event than current deicers this is countered by its lower toxicity and dermal permeability; due, perhaps in part, to its higher lipophilicity. Compound I is decomposed in the atmosphere at a rate comparable to current deicers. Like current deicers, it is not rapidly volatilized from aquatic systems. Upon ingestion, possibly at mouth pH but certainly at stomach pH, this compound is readily broken down into acetone and glycerol. Both of these compounds have relatively low toxicity and environmental concerns. The second of the compounds synthesized, compound III, exhibits a lower dermal permeability and dermal dose per event than any of the other compounds in this study. The decomposition products upon ingestion, which are glycerol and acetaldehyde, are also relatively non-toxic; acetaldehyde is even less toxic than acetone. Acetaldehyde is one of the metabolized products of ethanol.

Compound II was dismissed due to the formation of formaldehyde upon decomposition under mildly acidic conditions. Formaldehyde is a known toxic and carcinogenic agent and the use of formaldehyde adducts in this study was ceased for this reason. This concern aside, compound II exhibits similar properties to the other compounds in this study, with a lower dermal dose per event.

All three compounds were found to be soluble in jet fuel at the levels necessary for inhibiting the formation of ice; and closely paralleled the behavior of EGME and DiEGME(4). Accelerated fuel instability and incompatibility studies using ASTM method D5304-92 in JP-8 (7) showed negligible formation of solids (<0.01 mg) and no increased peroxidation.

CONCLUSION

Testing and evaluation of these new deicing compounds derived from sugars showed that they exhibited properties that make them ideal candidates for the next generation of deicing compounds. Both Compounds I and III are predicted to be environmentally benign and relatively nontoxic at the concentrations necessary for inhibiting ice formation. Compound I has been well characterized due to its current commercial applications, and the need for further investigation into the toxicity of Compound II is indicated. Other analogs from reduced sugars have been synthesized and evaluated and will be reported on in subsequent papers. The substituted forms of reduced sugars have the potential for the ideal combination of lipophilic and hydrophilic character necessary for deicing applications.

REFERENCES
(1)   Basak, S. C., Niemi, G. J. , Veith, G. D. J. of Mathematical Chemistry. 4, 185 (1990).
(2)   U.S. Department of Health & Human Services, Agency for Toxic Substances and Disease Registry, Tech. Rpt for Ethylene Glycol/Propylene Glycol Rprt 205-88-0608, May 1993.
(3)   Organic Synthesis Collective Volume 3, ed. E.C. Horning, pp 502-504, Wiley:New York, 1965.
(4)   Mushrush, G.W., Stalick, W.M., Beal, E.J., Basu, S.C., Slone, J.E., Cummings, Petroleum Science & Technology. 15(3,4), 237 (1997).
(5)   Meylan, W., Syracuse Research Corporation.DERMAL *for Windows*, Version 1.23, (1996).(a). MPBP *for Windows*, Version 2.51, (1996); (b). WSKOW *for Windows*, Version 1.20, (1996); (c). HENRY *for Windows*, Version 2.51, (1995); (d) AOP *for Windows*, Version 1.80, (1996); (e).KOC *for Windows*, Version 1.57, (1995); (f) *Estimation Program Interface for Windows*, Version 2.00, (1995).
(6)   Stirling, K. Q., Ripley, D. L. Partition Coefficients of Icing Inhibitors in JP-4 and JP-5 Jet Fuel, U. S. Department of Energy and Naval Air Propulsion Center, Final Report DE-FC22-83FE60149, October 1990.
(7)   ASTM ?Standard Test Method for Assessing Distillate Fuel Storage Stability by Oxygen Over pressure,? Annual Book of ASTM Standards; ASTM:Philadelphia, Part 0.05.01, ASTM D5304-92, (1992).
(8)   Sanderson, M. D. J. Pharm. Pharmacol. 11, 150 (1959) and 11, 446 (1959).

	Compound I	Compound II	Compound III
Dermal permeability K_p cm/hr	5.00×10^{-3}	6.94×10^{-4}	1.17×10^{-3}
Dermal dose per event (at concentration of 100 mg/cm^3 for 0.25 hr) in mg/cm^2	0.0430	0.0048	0.0079
log K_{ow} (lipophilicity)	1.07	-0.50	-0.09
Vapor pressure in mmHg	0.0647	0.2700	0.1140
Water solubility in mg/L	3.459×10^4	9.918×10^5	3.914×10^5
Henry's Law Constant in atm x m^3/mol	1.91×10^{-9}	1.08×10^{-9}	1.44×10^{-9}
OH rate constant in cm^3/molecules x sec	2.50420×10^{-11}	2.68248×10^{-11}	$2.99376 \times 10^{-}$
Atmospheric half-life in hrs.	5.125	4.785	4.287
Soil adsorption coefficient K_{oc}	1.00	1.00	1.00
Volatilization from model river in years (half-life)	60.30	94.712	75.62
Volatilization from model lake in years (half-life)	38.60	688.76	550.00
Biological Oxygen Demand in days (half-life)	2-15	2-15	2-15
LC$_{50}$ in ug/L for *Pimephales Promelas*	1.67×10^7	2.36×10^7	------
Bioconcentration factor for *Pimephales promelas*	1	1	1

Table 1. Compounds based upon the reduced sugar mannose

	Ethylene glycol mono-methyl ether (EGME)	Di(ethylene glycol) mono-methyl ether (DiEGME)
Dermal permeability K_p in cm/hr	4.98×10^{-4}	2.97×10^{-4}
Dermal dose per event (concentration of 100 mg/cm^3 for 0.25 hr) in mg/cm^2	4.66×10^{-3}	1.3×10^{-3}
log K_{ow} (lipophilicity)	-0.77	-1.18
Vapor pressure in mmHg	9.2200	0.2160
Water solubility in mg/L	1.000×10^6	1.000×10^6
Henry?s Law Constant in atm x m^3/mol OH rate constant in cm^3/ molecule x sec	4.19×10^{-8} 1.19983×10^{-11}	6.50×10^{-10} 2.60139×10^{-11}
Atmospheric half-life in hours	10.698	4.934
Soil adsorption coefficient K_{oc}	1.00	1.00
Volatilization from model river in years (half-life)	11.32	6660.27
Volatilization from model lake in years (half-life)	82.30	4.4844×10^5
Biological Oxygen Demand (BOD) in days (half-life)	2-16	2-16
LC_{50} in ug/L for *Pimephales promelas*	2.15×10^7	2.96×10^7
Bioconcentration factor (BCF) for *Pimephales promelas*	1	1

Table 2. Estimated values for current FSII additives